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AB-INITIO STUDIES OF N-O-F COMPOUNDS.

INTERNAL ROTATION IN HYDROXYLAMINE AND ITS FLUORINATED DERIVATIVES

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SUMMARY

Ab-initio molecular orbital theory at both the minimal and extended basis set levels have been applied to the study of internal rotation in hydroxylamine and its fluorinated derivatives. The computed energies are analyzed in terms of a Fourier-type expansion of the potential function. The total potential function $V(\phi)$ can be dissected into onefold (V_1), twofold (V_2) and threefold (V_3) components and plots of these components together with $V(\phi)$ are given for each of the molecules studied herein. Additionally geometry optimizations have been carried out as a function of the internal rotation angle ϕ (ϕ = : NOX dihedral angle) for H_2NOH and F_2NOF. For H_2NOH geometry optimizations are found to be less important than for F_2NOF. In general the fluorinated hydroxylamines prefer a trans-conformation (ϕ = 180°) while hydroxylamine itself adopts the cis-conformation (ϕ = 0°) largely as a result of a lower dipole interaction (V_1 term) in the cis-conformation.

INTRODUCTION

In the preceeding paper [1] we have examined the effect of fluorine on the geometries of hydroxylamine using ab initio molecular orbital theory. Herein we wish to examine the energy variation of hydroxylamine and its fluorinated derivatives as a function of rotation about the N-O bond. Molecular orbital theory has been used extensively in recent years to study the energy variation as a function of internal rotation in a number of small molecules [2]. Hydroxylamine has been studied by a number of workers [3-5] while Pople, et al. [5] have also examined the torsional barriers in N-fluorohydroxylamine and O-fluorohydroxylamine. These studies have employed either experimental or standard geometries, however, and it is well recognized that for certain molecules rotational barriers are highly sensitive to the proper initial geometry choice and may require a complete geometry optimization. In H_2O_2, for instance, a complete geometry optimization, together with the inclusion of polarization functions, was necessary for the accurate prediction of the torsional potential curve [6,7]. Gorenstein and Kar have recently shown that the torsional angles in dimethoxymethane and dimethyl phosphate are strongly coupled to the O-C-O (O-P-O) bond angles [8]. John and Radom [9] have also carried out geometry optimizations at various levels of approximation in their conformational studies of methyl vinyl ether and methyl formate.

In our previous study [1] we optimized the structure of hydroxylamine and its fluorinated derivatives. Herein we analyze the torsional potential curves of these molecules and also examine the effect of geometry optimizations of various conformations on these potential curves. We follow Pople et al. [5] in analyzing the rotational barriers. As these authors have shown the interpretation of rotational potential functions (in terms of electronic effects) can be aided by a separation of the total potential function into Fourier components. We will look at the decomposition of the potential function $V(\phi)$ for internal rotation about the N-O bond in hydroxylamine and its fluorinated derivatives. The function $V(\phi)$ may be separated into components,

$$V(\phi) = \sum_{n=1}^{3} V_n (1-\cos n\phi)/2$$

according to equation (1) for H_2NOH, H_2NOF, F_2NOH and F_2NOF:

$$V(\phi) = V_1(1-\cos\phi)/2 + V_2(1-\cos 2\phi)/2 + V_3(1-\cos 3\phi)/2 \quad (1)$$

For the asymmetric hydroxylamines such as FHNOH and FHNOF, equation (2) has been used for the Fourier expansion.

$$V(\phi) = V_1(1-\cos\phi)/2 + V_2(1-\cos 2\phi)/2 + V_3(1-\cos 3\phi)/2 \quad (2)$$
$$+ V_1' \sin\phi + V_2' \sin 2\phi$$

These truncated Fourier expansions generally give realistic descriptions of the potential functions.

Simple ab initio molecular orbital theory has been employed in this study using both the minimal STO-3G basis set [10] and the split-valence 4-31G basis set [11]. Calculation of the total energy at four values of the rotational angle ϕ(0°, 60°, 120°, 180°) enables the determination of the potential constants V_i in equation (1). For the determination of V_i (V_i') of equation (2) six values of the rotational angle ϕ have been used, viz., 0°, 60°, 120°, 180°, 240° and 330° [12]. We define ϕ here as the :NOX dihedral angle with the unshared electron pair corresponding to the fourth tetrahedral "ligand" around (N:).

RESULTS AND DISCUSSION

Table 1 records the relative conformational energies in kcal/mole for hydroxylamine and its fluorinated derivatives. The total energy for the minimum energy conformation of each molecule, except for H_2NOF and FHNOH, are recorded in Table 1 of the preceeding paper [1]. For H_2NOF and FHNOH we have used and recorded the total energies computed by Pople, et al. and recorded in Table 1 of reference 5. Figures 1-4 graphically depicts the total potential functions, $V(\phi)$, together with the Fourier components ($V_i(\phi)$ and $V_i'(\phi)$) for hydroxylamine and its fluorinated derivatives. The $V_i(\phi)$ and $V_i'(\phi)$ components of course all

TABLE 1

STO-3G and 4-31G Relative Energies (kcal/mol)^{a,b} for X_2NOX vs. ϕ

Molecule	Conformation (ϕ)	STO-3G	4-31G
H_2NOH	0°	0.0	0.0
	90°	7.0	9.5
	120°	8.2	10.7
	180°	5.1	8.2
F_2NOF	0°	0.9	5.6
	60°	4.7	8.2
	120°	7.2	10.7
	180°	0.0	0.0
H_2NOF	0°	-	4.6
	90°	-	17.0
	180°	-	0.0
FHNOH	25°	-	0.0
	115°	-	8.3
	175°	-	5.0
	270°	-	14.8
F_2NOH	0°	-	2.0
	60°	-	5.0
	120°	-	4.9
	180°	-	0.0
FHNOF	0°	-	5.7
	60°	-	10.9
	120°	-	21.0
	180°	-	0.0
	240°	-	8.9
	330°	-	10.9

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[a] The total energy for the minimum energy conformations are recorded in Table 1 of the preceeding paper.

[b] The total energies of H_2NOF and FHNOH are found in reference [5].

contribute to the location of the resultant maxima and minima for rotation about the N-O bond. In these figures the zero of energy corresponds to $V(\phi) = 0°$. The derived potential constants $V_i(V_i')$ from equations (1) and (2) are listed in Table 2. Before commenting individually on the figures we wish to point out that the study of Pople et al. [5] has demonstrated that generally 4-31G theory produces threefold barriers in moderate agreement with experiment, with the theoretical values being in general a little high. However, agreement

TABLE 2

Potential constants (V_i, V'_i kcal/mol) for internal rotation

Compound	V_1	V_2	V_3	V'_1	V'_2
H_2NOH(STO-3G)	6.48	4.45	- 1.38		
H_2NOH(4-31G)	8.87	5.40	- 0.67		
FHNOH(4-31G)	4.46	7.50	- 0.83	-4.09	-1.40
H_2NOF(4-31G)	-3.67	14.30	- 0.94		
FHNOF(4-31G)	-2.36	14.76	- 3.06	2.06	-4.69
F_2NOH(4-31G)	-1.42	5.25	- 0.61		
F_2NOF(STO-3G)	1.07	7.33	- 1.97		
F_2NOF(4-31G)	-2.07	8.87	- 3.53		

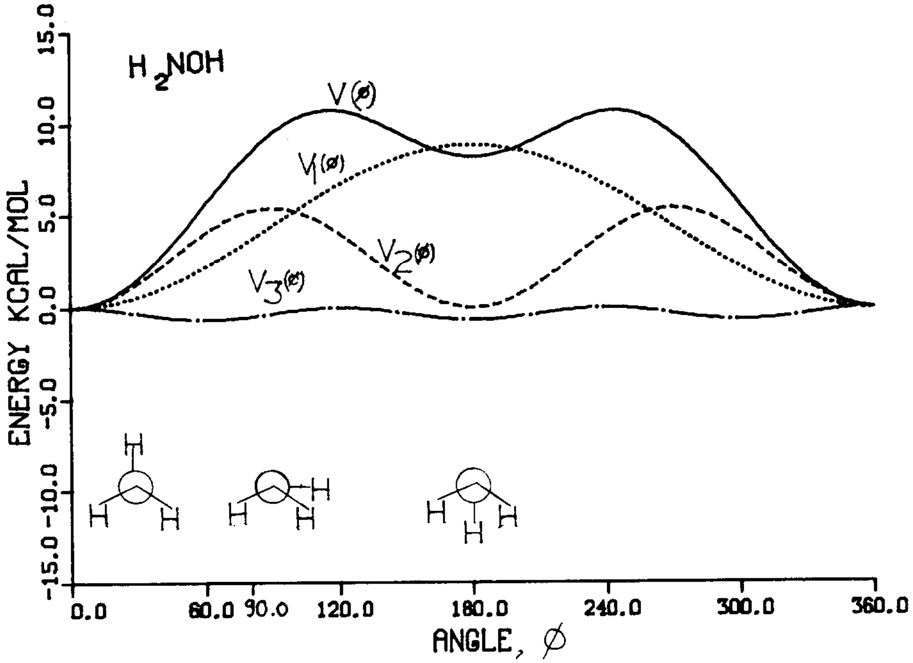
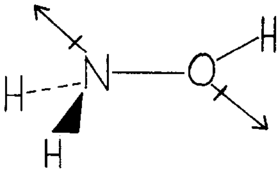


Figure 1 . Fourier decomposition of the potential function for H_2NOH (4-31G).

between theory and experiment for the V_2 and V_1 components is not as good. For instance there is a sizeable difference between V_1 and V_2 calculated and V_1 and V_2 experimental in the case of n-propyl fluoride [5b].

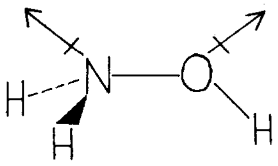
Figure 1 shows the potential function together with the components for hydroxylamine, according to 4-31G theory with the STO-3G results being rather similar. Both of these results are very similar to the 4-31G calculations of Pople, et al. [5] where standard geometries were employed. Similar to the findings of John and Radom [9] the STO-3G energies are seen to be somewhat smaller than the corresponding 4-31G values. According to Table 2 and Figure 1, the threefold component of the Fourier expansion (V_3) is relatively small and negative, indicating a preference for staggered over eclipsed bonds. The two-fold component (V_2) is large and positive favoring :NOH cis and trans forms in hydroxylamine. 4-31G calculated π overlap population (perpendicular to the NOH plane) for the N-O bond are consistent with this idea, viz. -0.04 for ϕ = 0° or 180° and -0.16 for the orthogonal conformation. The more positive values for the N-O π overlaps favor the planar conformation (See XIII - XVI of reference 5). V_1 is also large and positive and because of reduced dipole-dipole interactions in the cis-conformation (See I) as compared to the trans (see II), the former is favored by about 5 kcal/mol (STO-3G) - 8 kcal/mole (4-31G).



I

μ = 0.46D(STO-3G)

μ = 0.94D(4-31G)



II

μ = 2.89(STO-3G)

μ = 4.08D(4-31G)

Experimental evidence is in favor of cis and trans forms for hydroxylamine [13].

The present calculations when compared to the results of Pople, et. al. [5] suggest that geometry optimizations are not affecting the potential minima and maxima to any great extent for hydroxylamine. Thus, the barrier has decreased from 11.7 kcal/mol [5] to 10.5 kcal/mol largely as a result of the lowering of V_2. Even so, the geometric parameters of the various conformations do show significant variations as revealed by examining Table 3. All bond distances are seen to lengthen as one goes from the cis- to the trans-conformation. The HON angle increases about 3°(STO-3G) -5°(4-31G) for the same conformational comparison. As is usual with atoms of the first row of the periodic table, 4-31G theory characteristically overestimates bond angles. The bond angle variation with rotation in hydroxylamine is similar to that found in H_2O_2 where the optimized H-O-O angle in the trans-conformation is 100.2°, while the corresponding optimized bond angle in the cis or gauche conformation is 103.9° [6]. The O-O bond distance is also 0.025 Å longer in the cis conformation of H_2O_2 [6]. The larger HON angle in the trans conformation of hydroxylamine is reasonable since it minimizes the gauche HONH repulsions. It is probable that the barrier in hydroxylamine lies between the predicted STO-3G and 4-31G values at about 9 kcal/mol [9].

As discussed in reference [5] the effect of the electron-withdrawing fluorosubstituents is to increase the value of V_2, the increase being especially marked for H_2NOF. The V_1 term becomes less positive with fluorine substitution on nitrogen and is actually negative when the OH proton is replaced by fluorine leading to a trans potential minimum in H_2NOF which is 4.6 kcal/mol lower in energy than the cis-conformation with a barrier of 17 kcal/mol separating these two conformational minima. As Table 2 reveals there is generally an increase in the magnitude of V_3 with fluorine substitution. The negative V_1' for FHNOH suggests that conformations with ϕ between 0^o and 180^o are preferred over the $(360^o-\phi)$ conformations (see Figure 3 for definition of the direction of rotation).

TABLE 3

Geometry variations versus dihedral angle (ϕ) in H_2NOH

	ϕ							
	0°		90°		120°		180°	
Parameter	STO-3G	4-31G*	STO-3G	4-31G*	STO-3G	4-31G*	STO-3G	4-31G*
R(NO)+	1.424	1.44	1.42	1.44	1.42	1.44	1.434	1.44
R(OH)+	0.997	0.95	1.00	0.95	1.00	0.95	1.003	0.95
R(NH)+	1.039	1.00	1.04	1.00	1.04	1.00	1.041	1.00
∡NOH≠	101.6	106.1	102.2	108.7	104.2	110.4	104.4	111.0
∡ONH≠	107.5	106.2	109.6	107.1	110.9	107.9	109.1	108.5
			106.0		106.9			

*Bond lengths were optimized for only the minimum energy conformation (ϕ = 0°)

+Bond distances in Å. ≠Bond angles in degrees.

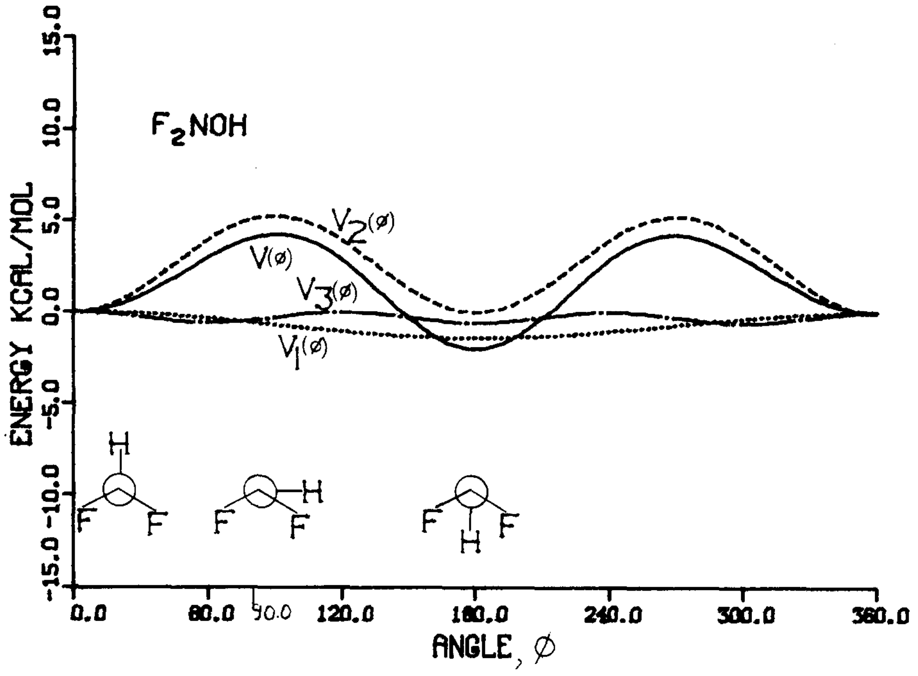


Figure 2. Fourier decomposition of the potential function for F_2NOH (4-31G, rigid rotor approximation).

Difluorination leads to the isomeric F_2NOH and FHNOF structures. Table 2 lists the V_i and Figure 2 presents the graphical analysis for F_2NOH. The values of V_3 and V_2 are seen to be not too much different from that in hydroxylamine. The V_1 component in F_2NOH is now, however, much less and, as is the case for H_2NOF, is negative and, as a result, the <u>trans</u>-conformation is favored. The <u>cis</u>-conformation lies 2 kcal/mol above the <u>trans</u>-form with a barrier at $\phi = 90^{\circ}$ of about 6 kcal/mol (trans - cis). Radom and Stiles [13] have discussed the effect of successive geminal fluorine substitutions on the magnitude of the rotational barriers in ethane. Thus the barriers in CH_3CH_3, CH_3CH_2F, CH_3CHF_2 and CH_3CF_3 are 2.93, 3.33, 3.18 and 3.25 kcal/mol, respectively [13]. The barrier lowering upon passing from CH_3CH_2F to CH_3CHF_2 was ascribed to a fluorine hyperconjugative effect. In F_2NOH the lower barrier compared to H_2NOH is largely due however to a reduction in the dipole-dipole term (V_1). The dipole moment changes only slightly in F_2NOH as a function of rotation about the N-O bond, viz., $\phi = 0^o$, $\mu = 2.5D$; $\phi = 180^o$, $\mu = 2.6D$. The reduction in the barrier between F_2NOH and H_2NOF on the other hand is seen to be due largely to a reduction of the two-fold component, presumably via nitrogen lone pair - OFσ^* interaction which favors the planar form more strongly in H_2NOF.

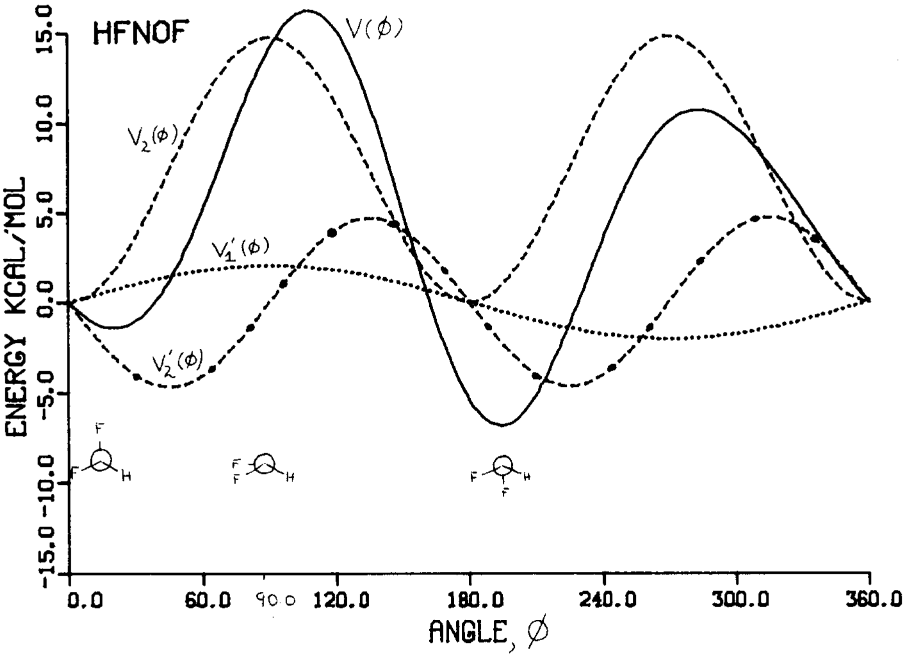


Figure 3. Fourier decomposition of the potential function for FHNOF (4-31G, rigid rotor approximation).

Table 2 lists the V_i (V_i) and Figure 3 presents the graphical results for FHNOF. For the sake of clarity the V_1 and V_3 components have been omitted in Figure 3. Similar to the findings for H_2NOF there is a large and positive V_2 component favoring cis ($\phi = 0^o$) and trans ($\phi = 180^o$) conformations, the latter being more stable by about 6 kcal/mol (negative V_1). Since V_1' is positive there is a preference for conformations between $\phi = 180^o - 360^o$ over conformations between 0° and 180° . The V_i' components in FHNOF lead to skewed minima occuring at about $\phi = 200^\circ$ and $\phi = 20^\circ$ with the former being favored by about 5 kcal/mol. The barriers occur at about $\phi = 280$ (~ 19 kcal/mol) and $\phi = 115^\circ$ (~23 kcal/mol). It should of course be pointed out that only the lowest energy conformation for F_2NOH and FHNOF ($\phi = 180$ was used) has been optimized so that the results presented in Figures 2 and 3 correspond to a rigid rotor approximation.

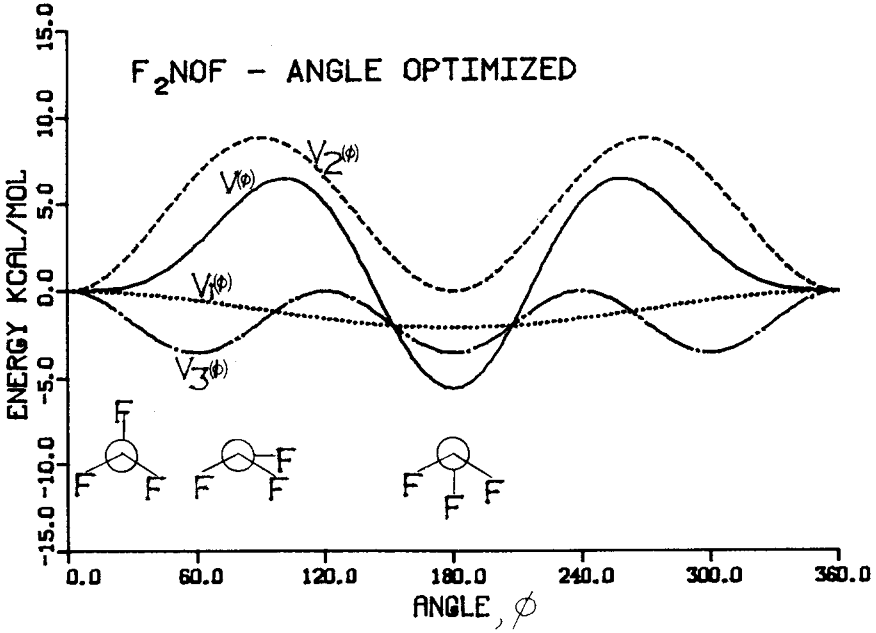


Figure 4 Fourier decomposition of the potential function for F_2NOF (4-31G, flexible rotor model).

Figure 4 illustrates the potential function $V(\phi)$, for F_2NOF while Table 2 lists the values of V_i. The agreement between the two basis sets as far as V_2 and V_3 is concerned is moderate, while there is serious disagreement between the two theoretical methods as far as the V_1 component is concerned (see Table 2). The STO-3G basis favors the cis-conformation (positive V_1) while 4-31G theory favors the trans-conformation (negative V_1). The discrepancy between the two computational methods for F_2NOF is not surprising

[1, 15]. Both theoretical bases favor V_2 as being the major contributor to the overall potential function. Thus, the 4-31G N-O π overlap population is 0.085 for the planar conformations ($\phi = 0^\circ$ and 180°) while it is - 0.10 for $\phi = 90^\circ$. Again the more positive overlap populations favoring the planar conformations.

We have found that geometry optimization (bond angles only) has a significant effect on the potential curves in F_2NOF. Optimization lowers the magnitude of all components from the rigid rotor results, but especially that of V_2. As a result the overall barrier is shifted from about 95° (rigid rotor) to about 115° (4) with the barrier height dropping from about 20 kcal/mol to about 12.5 kcal/mol. The energy difference between the cis and trans conformations is about 8.5 kcl/mol without optimization and about 5.6 kcl/mol with optimization of the bond angles. Table 4 records the variation of the bond angle as a function of ϕ for F_2NOF.

TABLE 4

Angle variations vs. dihedral angle (ϕ) in F_2NOF

$\phi =$	0°		120°		180°	
Parameter	STO-3G	4-31G	STO-3G	4-31G	STO-3G	4-31G
∡FON	103.0	102.7	107.2	109.3	106.9	107.6
∡ONF	105.8	105.6	104.9	104.8	107.5	108.5
			108.5	109.5		

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